

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization International Bureau



(43) International Publication Date  
15 July 2004 (15.07.2004)

PCT

(10) International Publication Number  
WO 2004/058876 A1

(51) International Patent Classification<sup>7</sup>: C08L 23/04, C08F 297/08 Rainer [DE/DE]; Augustaanlage 26, 68165 Mannheim (DE).

(21) International Application Number: PCT/EP2003/013867

(22) International Filing Date: 6 December 2003 (06.12.2003)

(25) Filing Language: English

(26) Publication Language: English

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(30) Priority Data:  
102 61 066.5 24 December 2002 (24.12.2002) DE  
60/445,163 5 February 2003 (05.02.2003) US

(84) Designated States (*regional*): ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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Published:

— with international search report

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

WO 2004/058876 A1

(54) Title: POLYETHYLENE BLOW MOULDING COMPOSITION FOR PRODUCING JERRY CANS

(57) Abstract: The invention relates to a polyethylene composition with multimodal molecular mass distribution, which is particularly suitable for the blow moulding of canisters having a volume in the range of from 2 to 20 dm<sup>3</sup> (l). The composition has a density in the range from 0.950 to 0.958 g/cm<sup>3</sup> at 23 °C and an MFR<sub>190/5</sub> in the range of from 0.30 to 0.50 dg/min. It comprises from 40 to 50 % by weight of a low-molecular-mass ethylene homopolymer A, from 25 to 35 % by weight of a high-molecular-mass copolymer B made from ethylene and from another olefin having from 4 to 8 carbon atoms, and from 24 to 28 % by weight of an ultrahigh-molecular-mass ethylene copolymer C.

## Title: Polyethylene blow moulding composition for producing jerry cans

The present invention relates to a polyethylene composition with multimodal molecular mass distribution, which is particularly suitable for blow moulding of canisters with a capacity in the range from 2 to 20 dm<sup>3</sup> (l) (jerry cans), and to a process for preparing this polyethylene composition in the presence of a catalytic system composed of a Ziegler catalyst and a co-catalyst, by way of a multistage reaction process composed of successive slurry polymerizations.

The invention further relates to the canisters produced from the molding composition by blow moulding.

Polyethylene is widely used for producing blow mouldings of all types requiring a material with particularly high mechanical strength, high corrosion resistance, and absolutely reliable long-term stability. Another particular advantage of polyethylene is that it also has good chemical resistance and is intrinsically a lightweight material.

EP-A-603,935 has previously described a blow moulding composition based on polyethylene having a bimodal molecular mass distribution, which is suitable for the production of mouldings with good mechanical properties.

US-A 5,338,589 describes a material with even broader molecular mass distribution, prepared using a high-mileage catalyst known from WO 91/18934, in which the magnesium alcoholate is used in the form of a gel-like suspension. Surprisingly, it has been found that the use of this material in mouldings, in particular in pipes, permits simultaneous improvement in properties which are usually contrary correlated in semicrystalline thermoplastics, these being stiffness and creep on the one hand and stress-crack resistance and toughness on the other hand.

However, the known bimodal products in particular have relatively low melt strength during processing. This means that the extruded parison frequently break in the molten state, making the extrusion process unacceptably sensitive to processing. In addition, especially when thick-walled containers are being produced, the wall thickness is found to be non-uniform, due to flow of the melt from upper regions into lower regions.

It is an objective of the present invention, therefore, to develop a polyethylene composition for blow moulding which can give a further improvement over all of the known materials in processing by blow moulding to canisters. In particular, the high melt strength of the moulding composition permits to run an extrusion process without parison disruption over a long time period, and the precisely adjusted swell ratio index of the composition permits optimization of wall-thickness control.

We have found that this objective is achieved by a composition as mentioned at the outset, the characterizing features of which are that it comprises from 40 to 50 % by weight of a low-molecular-mass ethylene homopolymer A, from 25 to 35 % by weight of a high-molecular-mass copolymer B made from ethylene and from another 1-olefin having from 4 to 8 carbon atoms, and from 24 to 28 % by weight of an ultrahigh-molecular-mass ethylene-1-olefin copolymer C, where all of the percentage data are based on the total weight of the composition.

The invention also relates to a process for preparing this composition in a cascaded slurry polymerization and to a process for producing, from this composition, canisters with a capacity in the range from 2 to 20 dm<sup>3</sup> (l) and with quite excellent mechanical strength properties.

The polyethylene composition of the invention has a density in the range from 0.950 to 0.958 g/cm<sup>3</sup> at 23 °C, and a broad trimodal molecular mass distribution. The high-molecular-mass copolymer B contains only small

proportions of other olefin monomer units having from 4 to 8 carbon atoms, namely from 0.2 to 0.5 % by weight. Examples of these comonomers are 1-butene, 1-pentene, 1-hexene, 1-octene, or 4-methyl-1-pentene. The ultrahigh-molecular-mass ethylene homo- or copolymer C also contains an 5 amount in the range from 1 to 2 % by weight of one or more of the above mentioned comonomers.

The composition of the invention has a melt flow index ISO 1133 in the range of from 0.30 to 0.50 dg/min, expressed in terms of MFR<sub>190/5</sub>, and a viscosity 10 number VN<sub>tot</sub> in the range of from 330 to 380 cm<sup>3</sup>/g, in particular from 340 to 370 cm<sup>3</sup>/g, measured according to ISO/R 1191 in decalin at 135 °C.

The trimodality is a measure of the position of the centers of gravity of the three individual molecular mass distributions, and can be described with the aid of 15 the viscosity number VN to ISO/R 1191 of the polymers formed in the successive polymerization stages. The relevant band widths for the polymers formed in each of the stages of the reaction are therefore as follows:

The viscosity number VN<sub>1</sub> measured on the polymer after the first 20 polymerization stage is identical with the viscosity number VN<sub>A</sub> of the low-molecular-mass polyethylene A and according to the invention is in the range from 60 to 80 cm<sup>3</sup>/g.

The viscosity number VN<sub>2</sub> measured on the polymer after the second 25 polymerization stage is not equal to VN<sub>B</sub> of the high-molecular-mass polyethylene B formed in the second polymerization stage, which can only be determined by calculation, but represents the viscosity number of the mixture of polymer A and polymer B. According to the invention, VN<sub>2</sub> is in the range from 160 to 200 cm<sup>3</sup>/g.

The viscosity number  $VN_3$  measured on the polymer after the third polymerization stage is not equal to  $VN_C$  of the ultra-high-molecular-mass copolymer C formed in the third polymerization stage, which can only be determined by calculation, but represents the viscosity number of the mixture of

5 polymer A, polymer B, and polymer C. According to the invention,  $VN_3$  is in the range of from 330 to 380  $\text{cm}^3/\text{g}$ , in particular from 350 to 370  $\text{cm}^3/\text{g}$ .

The polyethylene is obtained by polymerizing the monomers in slurry in the range of from 70 to 90 °C, preferably from 80 to 90 °C, at a pressure in the

10 range of from 0.15 to 1 MPa, and in the presence of a high-mileage Ziegler catalyst composed of a transition metal compound and of an organoaluminum compound such as triethylaluminum, triisobutylaluminum, alkylaluminum-chlorides or alkylaluminumhydrides. The polymerization is conducted in three stages, i.e. in three stages arranged in series, each molecular mass being

15 regulated with the aid of hydrogen feed.

The polyethylene composition of the invention may comprise other additives alongside the polyethylene. Examples of these additives are heat stabilizers, antioxidants, UV absorbers, light stabilizers, metal deactivators, compounds

20 which destroy peroxide, and basic costabilizers in amounts of from 0 to 10 % by weight, preferably from 0 to 5 % by weight, and also fillers, reinforcing agents, plasticizers, lubricants, emulsifiers, pigments, optical brighteners, flame retardants, antistats, blowing agents, or a combination of these, in total amounts of from 0 to 50 % by weight, based on the total weight of the mixture.

25 The composition of the invention is particularly suitable for the blow moulding process to produce canisters, by first plastifying the polyethylene composition in an extruder in the range from 200 to 250 °C and then extruding it through a die into a mould, where it is cooled and solidified.

The composition of the invention gives particularly good processing behavior in the blow moulding process to give canisters because it has a swell ratio index in the range of from 130 to 145 %, and the canisters produced therewith have particularly high mechanical strength because the moulding composition of the

5 invention has a notched impact strength (ISO) in the range from 14 to 17 kJ/m<sup>2</sup>. The stress-crack resistance (FNCT) is in the range from 150 to 220 h.

The notched impact strength<sub>ISO</sub> is measured according to ISO 179-1/1eA / DIN 53453 at 23 °C. The size of the specimen is 10 x 4 x 80 mm, and a V notch is

10 inserted using an angle of 45°, with a depth of 2 mm and with a notch base radius of 0.25 mm.

The stress-crack resistance of the molding composition of the invention is determined by an internal test method and is given in h. This laboratory method

15 is described by M. Fleißner in Kunststoffe 77 (1987), pp. 45 et seq., and corresponds to ISO/FDIS 16770, which has since come into force. In ethylene glycol as stress-crack-promoting medium at 80°C with a tensile stress of 3.5 MPa, the time to failure is shortened due to the shortening of the stress-initiation time by the notch (1.6 mm/razorblade). The specimens are produced

20 by sawing out three specimens of dimensions 10 x 10 x 90 mm from a pressed plaque of thickness 10 mm. These specimens are provided with a central notch, using a razorblade in a notching device specifically manufactured for the purpose (see Figure 5 in the publication). The notch depth is 1.6 mm.

## Example 1

Ethylene was polymerized in a continuous process in three reactors arranged in series. An amount of 1.3 Mol/h related to the titanium compound of a Ziegler catalyst prepared as specified in WO 91/18934, Example 2, and having the 5 operative number 2.2 in the WO, was fed into the first reactor together with 2.7 Mol/h triethylaluminum, as well as sufficient amounts of diluent (hexane), ethylene, and hydrogen. The amount of ethylene (= 6.75 t/h) and the amount of hydrogen (= 7.3 kg/h) were adjusted so that the percentage proportion of ethylene and of hydrogen measured in the gas phase of the first reactor were 10 18 % by volume and 70 % by volume, respectively, and the rest was a mix of nitrogen and vaporized diluent.

The polymerization in the first reactor was carried out at 84 °C.

15 The slurry from the first reactor was then transferred into a second reactor, in which the percentage proportion of hydrogen in the gas phase had been reduced between 10 to 12 % by volume, and an amount of 16.6 kg/h of 1-butene was added to this reactor alongside 4.35 t/h of ethylene. The amount of hydrogen was reduced by way of intermediate H<sub>2</sub> depressurization. 70 % by 20 volume of ethylene, 10.5 % by volume of hydrogen, and 1.1 % by volume of 1-butene were measured in the gas phase of the second reactor, the rest being a mix of nitrogen and vaporized diluent.

The polymerization in the second reactor was carried out at 82 °C.

25 The slurry from the second reactor was transferred to the third reactor using further intermediate H<sub>2</sub> depressurization to adjust the amount of hydrogen to 0.5 % by volume in the gas phase of the third reactor.

An amount of 67 kg/h of 1-butene was added to the third reactor alongside an amount of 3.90 t/h of ethylene. A percentage proportion of from 85 % by volume of ethylene, 0.5 % by volume of hydrogen, and 2.2 % by volume of 1-butene was measured in the gas phase of the third reactor, the rest being a mix of nitrogen and vaporized diluent.

The polymerization in the third reactor was carried out at 80 °C.

The long-term polymerization catalyst activity required for the cascaded process described above was provided by a specifically developed Ziegler catalyst as described in the WO mentioned at the outset. A measure of the usefulness of this catalyst is its extremely high hydrogen sensitivity and its uniformly high activity over a long time period of between 1 to 8 h.

15 The diluent was removed from the polymer slurry leaving the third reactor, and the material was dried and then pelletized.

Table 1 shown below gives the viscosity numbers and quantitative proportions  $w_A$ ,  $w_B$ , and  $w_C$  of polymer A, B, and C for the polyethylene moulding composition prepared in Example 1.

Table 1

|                               |       |
|-------------------------------|-------|
| Example No.                   | 1     |
| density [g/cm <sup>3</sup> ]  | 0.954 |
| MFR <sub>190/5</sub> [dg/min] | 0.40  |
| $w_A$ [% by weight]           | 45    |
| $w_B$ [% by weight]           | 29    |

|   |     |
|---|-----|
| W <sub>C</sub> [% by weight]            | 26  |
| VN <sub>1</sub> [cm <sup>3</sup> /g]    | 70  |
| VN <sub>2</sub> [cm <sup>3</sup> /g]    | 180 |
| VN <sub>tot</sub> [cm <sup>3</sup> /g]  | 360 |
| SR [%]                                  | 135 |
| FNCT [h]                                | 170 |
| NIS <sub>ISO</sub> [kJ/m <sup>2</sup> ] | 16  |

The abbreviations for physical properties in Table 1 have the following meanings:

5 - SR (= swell ratio) in [%] measured in a high-pressure capillary rheometer at a shear rate of 1440 s<sup>-1</sup>, in a 2/2 round-section die with conical inlet (angle = 15°) at 190 °C.

10 - FNCT = stress-crack resistance (Full Notch Creep Test) tested using the internal test method of M. Fleißner, in [h],

- NIS<sub>ISO</sub> = notched impact strength measured to ISO 179-1/1eA / DIN 53453 in [kJ/m<sup>2</sup>] at 23 °C.

We claim

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1. A polyethylene moulding composition with multimodal molecular mass distribution, which has a density in the range of from 0.950 to 0.958 g/cm<sup>3</sup> at 23 °C and an MFR<sub>190/5</sub> in the range of from 0.30 to 0.50 dg/min, and which comprises from 40 to 50 % by weight of a low-molecular-mass ethylene homopolymer A, from 25 to 35 % by weight of a high-molecular-mass copolymer B made from ethylene and from another 1-olefin having from 4 to 8 carbon atoms, and from 24 to 28 % by weight of an ultrahigh-molecular-mass ethylene copolymer C, wherein all of the percentage data are based on the total weight of the moulding composition.
- 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170 175 180 185 190 195 200 205 210 215 220 225 230 235 240 245 250 255 260 265 270 275 280 285 290 295 300 305 310 315 320 325 330 335 340 345 350 355 360 365 370 375 380 385 390 395 400 405 410 415 420 425 430 435 440 445 450 455 460 465 470 475 480 485 490 495 500 505 510 515 520 525 530 535 540 545 550 555 560 565 570 575 580 585 590 595 600 605 610 615 620 625 630 635 640 645 650 655 660 665 670 675 680 685 690 695 700 705 710 715 720 725 730 735 740 745 750 755 760 765 770 775 780 785 790 795 800 805 810 815 820 825 830 835 840 845 850 855 860 865 870 875 880 885 890 895 900 905 910 915 920 925 930 935 940 945 950 955 960 965 970 975 980 985 990 995 1000 1005 1010 1015 1020 1025 1030 1035 1040 1045 1050 1055 1060 1065 1070 1075 1080 1085 1090 1095 1100 1105 1110 1115 1120 1125 1130 1135 1140 1145 1150 1155 1160 1165 1170 1175 1180 1185 1190 1195 1200 1205 1210 1215 1220 1225 1230 1235 1240 1245 1250 1255 1260 1265 1270 1275 1280 1285 1290 1295 1300 1305 1310 1315 1320 1325 1330 1335 1340 1345 1350 1355 1360 1365 1370 1375 1380 1385 1390 1395 1400 1405 1410 1415 1420 1425 1430 1435 1440 1445 1450 1455 1460 1465 1470 1475 1480 1485 1490 1495 1500 1505 1510 1515 1520 1525 1530 1535 1540 1545 1550 1555 1560 1565 1570 1575 1580 1585 1590 1595 1600 1605 1610 1615 1620 1625 1630 1635 1640 1645 1650 1655 1660 1665 1670 1675 1680 1685 1690 1695 1700 1705 1710 1715 1720 1725 1730 1735 1740 1745 1750 1755 1760 1765 1770 1775 1780 1785 1790 1795 1800 1805 1810 1815 1820 1825 1830 1835 1840 1845 1850 1855 1860 1865 1870 1875 1880 1885 1890 1895 1900 1905 1910 1915 1920 1925 1930 1935 1940 1945 1950 1955 1960 1965 1970 1975 1980 1985 1990 1995 2000 2005 2010 2015 2020 2025 2030 2035 2040 2045 2050 2055 2060 2065 2070 2075 2080 2085 2090 2095 2100 2105 2110 2115 2120 2125 2130 2135 2140 2145 2150 2155 2160 2165 2170 2175 2180 2185 2190 2195 2200 2205 2210 2215 2220 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5. A polyethylene composition as claimed in one or more of claims 1 to 4, which has a swell ratio in the range of from 130 to 145 %, and a notched impact strength (ISO) in the range of from 14 to 17 kJ/m<sup>2</sup>, and a stress-crack resistance (FNCT) in the range of from 150 to 220 h.
- 10 6. A process for producing a polyethylene composition as claimed in one or more of claims 1 to 5, in which the monomers are polymerized in suspension at a temperature in the range of from 20 to 120 °C, at a pressure in the range of from 0.15 to 1 MPa, and in the presence of a high-mileage Ziegler catalyst composed of a transition metal compound and of an organoaluminum compound, which comprises conducting polymerization in three stages, where the molecular mass of the polyethylene prepared in each stage is regulated with the aid of hydrogen.
- 15 7. A process as claimed in claim 6, wherein the hydrogen concentration in the first polymerization stage is adjusted so that the viscosity number VN<sub>1</sub> of the low-molecular-mass polyethylene A is in the range from 60 to 80 cm<sup>3</sup>/g.
- 20 8. A process as claimed in claim 6 or 7, wherein the hydrogen concentration in the second polymerization stage is adjusted so that the viscosity number VN<sub>2</sub> of the mixture of polymer A and polymer B is in the range from 160 to 200 cm<sup>3</sup>/g.
- 25 9. A process as claimed in any of claims 6 to 8, wherein the hydrogen concentration in the third polymerization stage is adjusted so that the viscosity number VN<sub>3</sub> of the mixture of polymer A, polymer B, and polymer C is in the range of from 330 to 380 cm<sup>3</sup>/g, in particular of from 340 to 370 cm<sup>3</sup>/g.

10. The use of a polyethylene composition as claimed in one or more of claims 1 to 5 for producing canisters with a capacity in the range from 2 to 20 dm<sup>3</sup> (I), where the polyethylene composition is first plasticized in an extruder in the range from 200 to 250 °C and is then extruded through a die into a mould, where it is first blown up and then cooled and solidified.

\* \* \* \* \*

## INTERNATIONAL SEARCH REPORT

PCT/EP 03/13867

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 7 C08L23/04 C08F297/08

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
 IPC 7 C08L C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages                      | Relevant to claim No. |
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents:

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- \*O\* document referring to an oral disclosure, use, exhibition or other means
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- \*&\* document member of the same patent family

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| Date of the actual completion of the international search<br><br>25 March 2004   | Date of mailing of the international search report<br><br>31/03/2004 |
| Name and mailing address of the ISA<br><br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax: (+31-70) 340-3016 | Authorized officer<br><br>Van Golde, L                               |

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PCT/EP 03/13867

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